

Effects of Alloying Elements on Cobalt Silicide Formation

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Abstract

We demonstrate that alloying elements can substantially affect the formation of cobalt silicide. A comprehensive study of phase formation was performed on 23 cobalt alloys with alloying element concentrations ranging from 1 up to 20 at.%. Using *in-situ* characterization techniques in which x-ray diffraction and elastic light scattering are measured simultaneously, we follow the formation of the silicide phases and the associated variation in surface roughness in real time during rapid thermal annealing (RTA). For pure cobalt silicide, we detect the formation of all stable silicide phases (Co_2Si , CoSi and CoSi_2) as well as the abnormal grain growth in the Co film observed at lower temperatures and the thermal degradation of the silicide at higher temperatures. The effect of the various additives on the formation temperatures was determined. By selecting an alloy at a given composition, we can significantly modify the process window for silicide formation, and influence the nucleation and kinetics of formation.

Introduction

Because of the ease of formation in small dimensions, cobalt silicide has matured into an important alternative to titanium silicide for contacts to silicon in CMOS devices. It is, however, much more sensitive to impurities and to the preparation of the silicon surface before deposition, and typically leads to rougher interfaces resulting in larger leakage currents. Successful formation of cobalt silicide now relies on a thin suboxide at the Si/Co interface that affects the diffusion during annealing sufficiently to limit the epitaxial faceting between the silicon and the disilicide, and limit the interface roughness [1]. As the critical dimensions are reduced, it becomes increasingly important to understand the role impurities play on the formation kinetics and to affect the formation of the silicide in an attempt to control its roughness. In current manufacturing process, the silicide formation (self aligned) is performed in two stages. The CoSi is formed first, followed by a selective etch that removes any unreacted material,

in turn followed by a second anneal that forms the low resistivity CoSi_2 . The variations in formation temperature for CoSi and CoSi_2 are thus critical for possible implementation in current or future devices.

Experimental Conditions

In the current study, Si(100) substrates were cleaned in diluted HF acid, blown dry without rinse and loaded directly into the sputter deposition system. A binary Co alloy layer, 8 nm thick, was co-sputtered from two elemental targets and then capped with a 20 nm TiN film after an air break. The 23 cobalt alloys shown in Figure 1 were originally deposited at average additive concentrations of 2 and 5.6 at. %, as determined using Rutherford backscattering spectroscopy (RBS). In a second series of samples, ten alloys were selected for a study covering a larger composition range (up to 20 at.%). They were also capped with 20 nm of TiN, in this case without air break.

The annealing experiments were performed at the NSLS X20C beamline, where we follow the formation

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		8 nm Co (X at. % element)									
										xiii	xiv
										Al	C
iv	v	vi	vii	viii	ix	x	xi	xii		Si	
Ti	V	Cr	Mn	Fe	Co	Ni	Cu			Ge	
Zr	Nb	Mo		Ru	Rh	Pd				Sn	
	Ta	W	Re		Ir	Pt					

Figure 1. List of additive elements used for the first series of samples processed. Each Co alloy layer contained 8 nm of Co and either 2 or 5.6 at.% of the additive element. These films were capped with 20 nm of TiN after an air break.

of different phases via the development of their characteristic diffraction patterns [2]. We selected an energy of 6.9 keV (0.180 nm) using a multilayer monochromator with a 1.5% energy resolution that provides an x-ray flux greater than 10^{13} photons/s. The combination of the high x-ray photon flux with a linear, position-sensitive detector allows both fast data acquisition during rapid thermal anneals (RTA) and observation of very thin films. In the current configuration, a diffraction spectrum (10° in 2θ) from a 10 nm metal film can be acquired in less than 100 ms. The experimental apparatus is so designed [3] that one can simultaneously observe the evolution of the surface conditions via the elastic scattering of monochromatic light. These measurements of roughness are made from laser light of wavelength 633 nm, at an incident angle of 65° and scattered angles of -20° and 52° (with two detectors) providing information on length scales of about 0.5 μm and 5 μm , respectively. The samples are squares cut from Si wafers with dimensions of approximately 1.5 cm on the side. After multiple evacuations of the annealing chamber, purified N_2 or He with oxygen contamination below the part-per-trillion level (ppt) flows through the chamber during the anneal. The temperature measurements are calibrated using metal silicon eutectics and are precise to $\pm 3^\circ\text{C}$. Further experimental details are provided in [2-4].

Results and Discussion

Figure 2 reveals the reaction of an uncapped 8 nm Co film deposited on an undoped Si(100) substrate as measured with light scattering (Fig. 2a) and x-ray diffraction (Fig. 2b). The x-ray peak at about 53° in Fig. 2b is that of hexagonal Co (002). The observable change above 300°C is a consequence of the abnormal growth of grains with the (001) orientation [5]. A slight shift in angular position coincides with strain relief during grain growth. At higher temperature, the shift of the Co(002) peak towards higher 2θ corresponds to the Co_2Si phase formation. The occurrence of the CoSi is barely detectable. Between 500°C and 600°C one can discern a faint trace at about 54° and another above 59° ; these are respectively the (210) and (211) diffraction lines of CoSi. The very weak intensity of these two peaks is due to the highly random orientation of that phase. The peak at about 57° above 600°C is the (220) diffraction line of CoSi_2 . Changes in both light scattering signals in Figure 2a coincide well to the formation of the disilicide. The roughening observed on the 0.5 μm lengthscale is typical of TiSi_2 , CoSi_2 and NiSi_2 formation where most of the roughness develops on lateral lengthscales larger than 200 nm due to the importance of nucleation in the disilicide formation[6]. The peak observed in the longer lengthscale signal (5 μm) is a result of large lateral non-uniformity during forma-

tion. At the mid point of the formation, areas of CoSi and CoSi_2 coexist on these lengthscales generating a temporary roughness that disappears as the transformation completes.

The changes in phase formation that can be observed when the Co is alloyed are illustrated in Figure 3 with several examples. We selected concentrations of 15 at.% (from the second set of samples) in order to show how drastic the variations can be. Figure 3a represents the 3°C/s ramp anneal of a pure Co film capped with TiN. The x-ray data are similar to that of Figure 2b except that the Co(002) peak is narrower allowing a clearly visible metal-rich Co_2Si phase which extends from 430 to 490°C , at which point the CoSi forms. The formation of the disilicide occurs around 620°C as seen by the increase of the (220) diffraction line of CoSi_2 at slightly more than 55° . In Figure 3b, the Co is alloyed with 15 at.% Ge. For such a concentration, the first striking difference compared to the pure Co case is that the Co(002) and Co_2Si (301) intensities completely disappear. Through the intensity contour, one barely detects the formation of the monosilicide, but it occurs at a temperature similar to that of the pure Co case. Another difference is the formation temperature of the

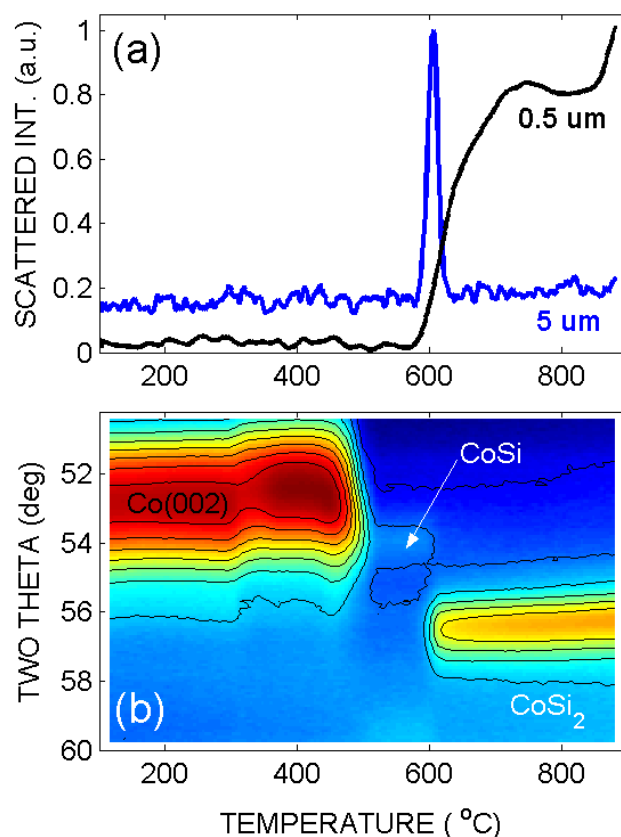


Figure 2. (a) Elastic light scattering from 0.5 μm and 5 μm length scales together with (b) x-ray diffraction measurement performed in situ during annealing (3°C/s) of a 8 nm Co layer deposited on Si(100).

disilicide, which increases by more than 100°C. Note that the increase in $\text{CoSi}_2(220)$ intensity is even more abrupt than for the pure Co case. The effect of adding 15 at.% Re to the Co is presented in Figure 3c. In this case, the (002) texture of the starting Co peak is much more intense and is present up to 600°C, which is more than 150°C higher than the disappearance of this peak in the pure Co case. Moreover, at this high temperature, the formation sequence does not show the presence of the metal rich silicide phase. The disilicide formation is also moved to higher temperatures but note that the increase in intensity is not as sudden as for Figures 3a and 3b suggesting a significant change in the kinetics. The addition of 15 at. % of Ni to the Co (Figure 3d) reduces the initial (002) texture of the Co without eliminating it completely. The metal rich and monosilicide phases also form at similar temperatures as for the pure Co film. In contrast to the Ge and Re additions, the Ni reduces the formation temperature of CoSi_2 by about 75°C. Note that as with the Re addition, the intensity of the CoSi_2 peak increases gradually with temperature.

With the same x-ray technique used in Figures 2 and 3, we measured the formation sequence of the

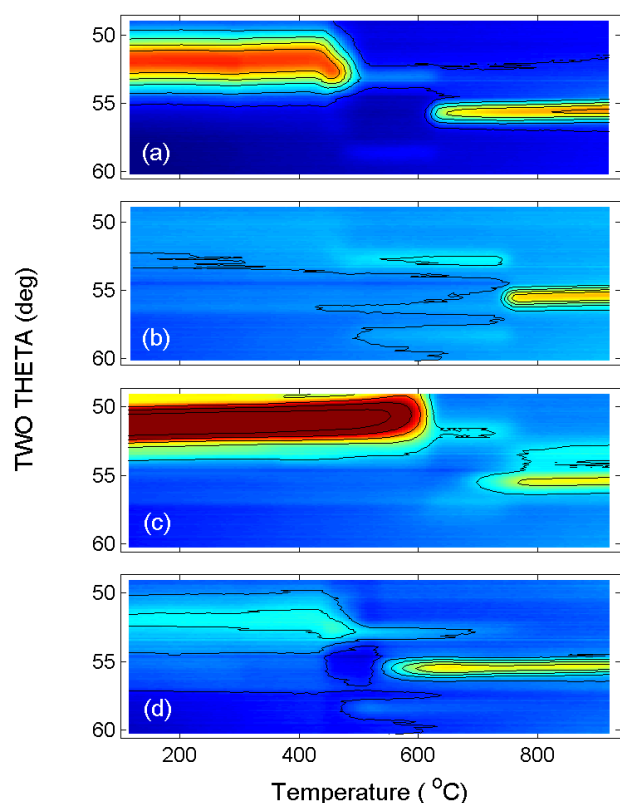


Figure 3. In situ x-ray diffraction measurements during annealing of 8nm thick films: (a) pure Co, (b) Co(15 at.% Ge), (c) Co(15 at.% Re) and (d) Co(15 at.% Ni). Samples were deposited on Si(100) substrates and capped with 20nm of TiN.

silicides on the set of 23 samples deposited at average concentrations of 2 and 5.6 at.%. The formation temperatures are selected as the temperatures for which the silicide x-ray diffraction intensity is increasing at the fastest rate. If texture variations in the silicide layer are not important as the phase forms, this temperature corresponds to the maximum rate in phase formation. Both the formation temperatures of CoSi and CoSi_2 are presented in Figure 4 by showing the range of existence of the CoSi phase when the temperature is continuously ramped at 3°C/s. The results are presented following the structure of the periodic table. Figures 4a, 4b and 4c represent respectively the first, second and third row of the transition elements (columns 4 to 11 in the periodic table). Figure 4d shows the formation temperatures for the selected elements in columns 13 and 14, which are the elements that are expected to take the position of Si in the CoSi_2 compound. The two dotted lines across each plot represent the formation temperatures of CoSi and CoSi_2 measured from the pure Co film. For CoSi formation (the lower end of each bar), it is clear that none of the selected elements and concentrations leads to a significant decrease in formation temperature while some of the measured increases were as large as 100°C (Mo, W). The formation temperatures of CoSi_2 (higher end of each bar) also vary by more than 100°C, with the lowest formation temperature being observed for Ni additions while the highest one was measured with Ge additions. While most elements lead to an increase in the formation temperature of the disilicide that is more significant with a larger concentration of the additive, Ni, Cu and, Pd lead to a decrease in CoSi_2 formation temperature.

The formation temperatures for the second set of Co alloy samples are shown in Figure 5. The samples were annealed in the same conditions. For each additive element, the temperature range over which the monosilicide is present has been highlighted. As the concentration of additive element is increased, different behaviors are observed. The monosilicide formation temperature is either relatively independent of alloying (Si, Ni, Ge), increases monotonically (Ti, Re, Cr, V, Ta) or shows a maximum with increasing concentration (Ir, Rh). None of the ten additive elements significantly decreases the formation temperature of CoSi . For the disilicide formation temperature, monotonic increases were observed for Ti, Ge, Ir, Rh, Re and Cr. The largest increase was recorded for Ge additions. Alloying the Co with Ta generated little or no changes in CoSi_2 formation temperature. In the case of Ni, the formation was facilitated as the concentration increased to 20 at.%. Lastly, alloying Co with V leads to a non-monotonic behavior where the CoSi_2 formation temperature increased significantly at low V concentration and then showed a reverse tendency by decreasing as

the V concentration kept increasing. The result of these measured variations shows that the process window for silicide formation (in electronic circuit fabrication) changes significantly and in different ways with different alloying elements.

One factor that has proven useful in predicting changes in disilicide formation temperatures with alloying is the miscibility of the respective silicide phases. As the new silicide phase forms, changing from phases that are miscible to phases that are not (or vice versa) will lead to changes in the entropy of mixing that directly affect nucleation. The result of this is that silicide phases that are miscible are favored over the ones that do not intermix. This entropy of mixing effect on the nucleation of the disilicide has been described earlier using the (Co,Ni)-Si system [7] and more recently in a systematic study using various metal interlayers and capping layers in the Co - Si system [8, 9].

In the case of Cr, Mn, Fe, Ge, Ru, Rh and Re, the monosilicides are fully miscible and the disilicides are not. For Rh and Mn, the disilicide phases have not been measured (not part of current phase diagrams). In the case of Ge, we refer to the miscibility and immiscibility of silicides and germanides (CoSi / CoGe and CoSi_2 / CoGe_2) since the Ge replaces the Si, not the Co. For these elements, the change in entropy is negative and has the effect of increasing the barrier for nucleation. For all of these elements (as predicted recently [8, 9]), the formation of the disilicide moved towards higher temperature. One should however be careful about attributing these changes to the entropy of mixing alone. Indeed, the comparison of the disilicide formation with pure Co (Figure 4a) and with 15 at.% Ge (4b) shows not only the increase in temperature but also a very sharp formation for the Ge case suggesting a nucleation controlled reaction. For the Re addition however (Figure 4c, 15 at.%), the transformation temperature is also raised but the formation of the disilicide is much more gradual. A gradual formation is not expected if the formation remains purely nucleation controlled, suggesting that other factors such as interfacial energies, stress and enthalpy changes due to alloying are also contributing.

In the case of Co-Ni, where the monosilicides have different crystal structures and are not completely miscible while the disilicides are miscible, the entropy increases at the transformation leading to a decrease of the nucleation barrier. As a result, the disilicide formation temperature is reduced. One can also notice in the

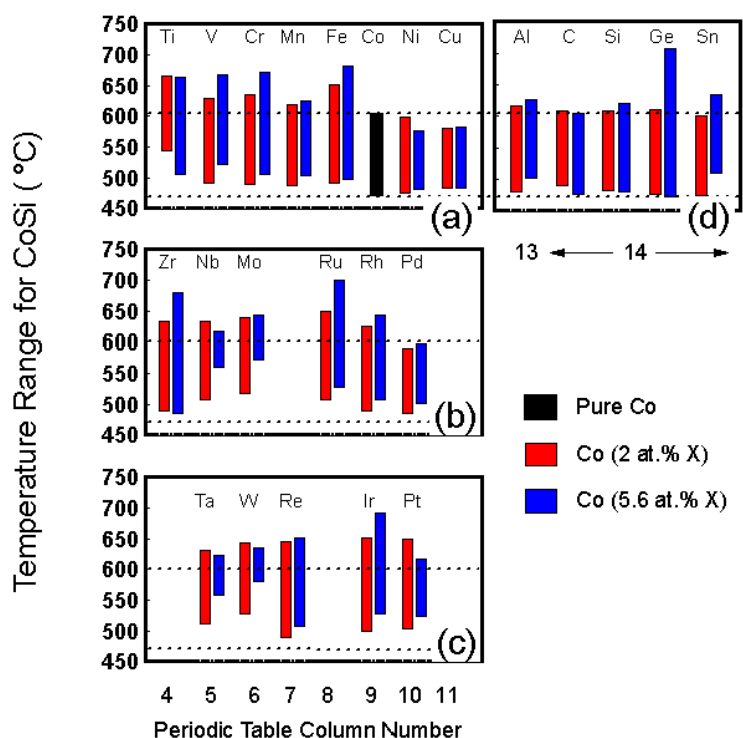


Figure 4. Temperature range over which the CoSi phase exists when samples are annealed at 3°C/s . The bottom and top of each bar correspond to the formation of CoSi and CoSi_2 respectively. All alloys were tested at two concentrations averaging 2 and 5.6 at.%. For (a), (b) and (c), the data is structured as in the transition elements in the periodic table. In (d), we regroup the elements from columns 13 and 14 (expected to replace Si in CoSi_2).

increase of $\text{CoSi}_2(220)$ x-ray intensity in Figure 4a (pure Co) and 4d (Co 15 at.% Ni) that by comparison, the formation of the disilicide is much slower in the case of the Ni addition. This suggests that the nucleation barrier may be low enough that the formation of the disilicide is controlled mainly by diffusion. Note here that even if the monosilicides are not completely miscible, there is a certain degree of solubility of Ni in CoSi and Co in NiSi [10]. At 800°C , more than 20% of the Co atoms could be replaced by Ni atoms. We expect the solubility to be slightly lower around 600°C , the temperature at which the monosilicide forms. This limited solubility should, in effect, reduce the contribution of the mixing entropy to the decrease of the nucleation barrier. In particular, for small concentrations of Ni, where the additive element is in solution in both the mono and disilicide, the current argument does not stand. The decrease in formation temperature and nucleation barrier must be attributed to other mechanisms such as variations in enthalpy or surface energies. The same argument can also be applied to the Fe silicide case (mentioned above) where the monosilicides are miscible but the disilicides are not.

At 800°C, a solubility of about 6at.% has been reported for Fe in CoSi_2 . We measure an increase of about 50°C for only 2 at.% of Fe, well below the solubility limit. Here again, we believe that variations in enthalpies and surface energies are dominating the observed variations.

Conclusions

Using *in-situ* characterization techniques in which x-ray diffraction and elastic light scattering are measured simultaneously, phase formation sequences and variations in surface roughness were measured during annealing of Co alloy films on Si(100) substrates. The binary alloys were co-sputtered covering a range of concentrations for 23 different additive elements. Not surprisingly, the effects of alloying can vary drastically. Differences in phase formation temperatures, sensitiv-

ity to abnormal grain growth in the cobalt, cobalt and silicide texture, as well as sensitivity to impurities, have been observed. The large variations in formation temperature for the disilicide can be explained from multiple factors depending on the additive element selected. For example, miscibility and entropy of mixing are critical in understanding the nucleation. Surface energy arguments (i.e. roughness, segregation, epitaxy,...) can be dominant in some cases and be influenced by slight amounts of oxygen at the surface or interface. The comparison of formation temperatures of silicide phases and resistivity performed in this study allows us to select candidate alloys for implementation. Note as well that the extensive study permits the tailoring of material properties. This degree of control will become critical as the device size is further reduced and new device structures are implemented.

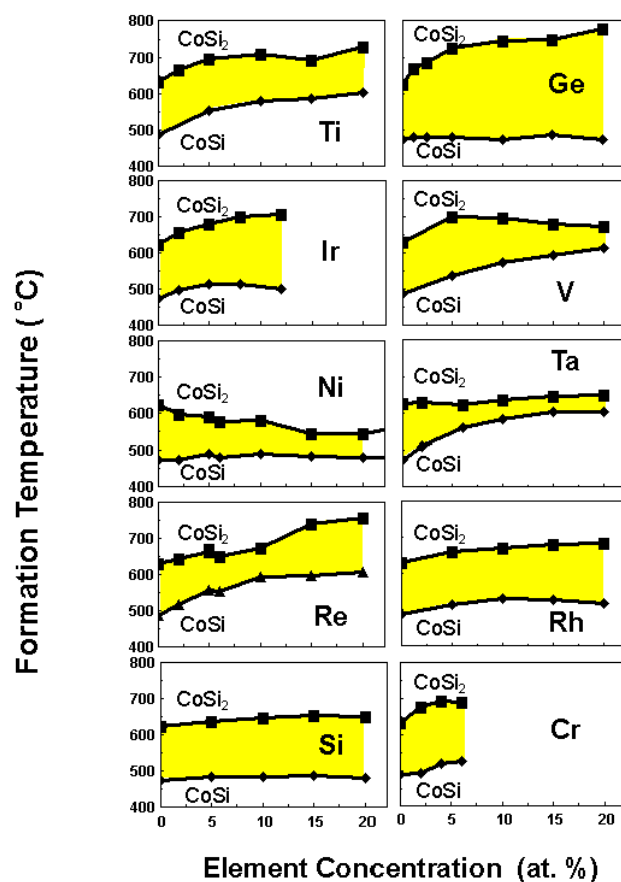


Figure 5. Formation temperature of CoSi and CoSi_2 for the 10 alloys selected in the second study. Alloys were deposited on Si(100) substrates and annealed at 3°C/s. The yellow areas represent the temperature range over which the CoSi phase exists.

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